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VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF ZINC.

FIRST PAPER : THE ANALYSIS OF ZINCIC BROMIDE.

BY THEODORE WILLIAM RICHARDS AND ELLIOT FOLGER ROGERS.

Presented April 10, 1895.

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INTRODUCTION.

IN an account of a recent investigation on the occlusion of gases by the oxides of metals * it was shown that zincic oxide, in common with cupric and magnesic oxides, has the power of retaining important quantities of oxygen and nitrogen gases, even at very high temperatures. Hence it was evident that all determinations of the atomic weight of zinc depending upon the conversion of the metal into the oxide through the ignition of the nitrate must be influenced by a constant error, which has the tendency to make the results lower than the true value. In consideration of this fact, it becomes very important to review all of the results thus far obtained regarding the atomic weight of zinc, in order to determine how seriously the error in question may influence our accepted value. A chronological list † of the accessible data is given below.

* These Proceedings, XXVIII. 200, Richards and Rogers.

† Much assistance in preparing the list has been obtained from the works of Clarke, Meyer and Seubert, and others. The results have been recalculated with the assumption of the following atomic weights: O = 16, C = 12.002 Cl = 35.456, Aq = 107.93, H = 1.0075.

1809.	Gay Lussac, Mém. d'Arceuil, II. 174	65.55
1811.	Berzelius, Pogg. Ann., VIII. 184	65.57
1842.	Jacquelain, An. de Chim. et de Phys. [3.], VII. 204 .	66.24
1844.	Favre, An. de Chim. et de Phys. [3.], X. 163 . . .	65.99
1844.	Erdmann, Berz. Jahresber., XXIV. 132, and Pogg. Ann., LXII. 612	65.05
1883.	Pelouze and Fremy, Chem., p. 55	65.07
1883.	Baubigny, Comptes Rendus, XCVII. 906	65.41
1883.	Marignac, Archiv. Sci. Phys. et Nat. [3.], X. 5, 193 .	65.30
1885.	Van der Plaats, Comptes Rendus, C. 55	?
1887.	Reynolds and Ramsay, J. Ch. Soc. Trans., LI. 854 .	65.67
1888.	Morse and Burton, Am. Chem. Journ., X. 311 . . .	65.27
1889.	Gladstone and Hibbert, J. Ch. Soc. Trans., LV. 443 .	65.44

The various results have been reached:—

1. By converting a known weight of metallic zinc into the oxide (Berzelius, Jacquelain, Erdmann, Morse and Burton).
2. By the evolution of hydrogen from acids by metallic zinc, the hydrogen being either measured or burned, (Jacquelain, Favre, Van der Plaats, Reynolds and Ramsay).
3. By the conversion of a salt of zinc into zincic oxide through ignition (Favre, zincic oxalate; Pelouze, zincic lactate; Baubigny, zincic sulphate).
4. By the determination of the electrolytic equivalent of zinc (Gladstone and Hibbert).
5. By analysis of a haloid salt of zinc (Marignac.)

The work of Morse and Burton by the first method is so far superior to the previous determinations made in the same way, that the older ones may be wholly neglected. The two or three possibilities of infinitesimal error, such as the chance that the zinc might contain impurities taken from the glass used for its distillation, may be wholly neglected when compared with the great error due to the occlusion of nitrogen and oxygen. As the amount of this error is dependent upon the physical condition of the zincic oxide, it is impossible to make an accurate correction except by the actual determination of the gas in the oxide remaining from the determinations. From our own experiments* it would appear that a gram of zincic

* These Proceedings, XXVIII. 200.

oxide obtained from the nitrate usually contains about 0.00057 gram of occluded gas; upon this basis Morse and Burton's result would become 65.458 instead of 65.269.

In considering the results obtained by the second method the results of Favre and Jacquelain may be rejected at once. Of Van der Plaat's results it is necessary to state only that some error must have crept in while recording his data, for it is inconceivable that 6.6725 grams of zinc should yield only 1.1424 litres of hydrogen. The work of Reynolds and Ramsay was much more careful and detailed; but the results varied very widely. Hydrogen evolved from very pure zinc was measured, with many precautions; but after the rejection of thirty-four experiments eleven more gave a value of 65.24, and still five more gave 65.47 as the atomic weight of zinc. Since the publication of their work many investigations have shown that the density of hydrogen is greater than the value assumed at that time. If a litre of the gas weighs 0.9001* gram, and the atomic weight of hydrogen is taken as 1.0075 ($O = 16.000$) the atomic weight of zinc deduced from Reynolds and Ramsay's experiments becomes about 65.63.

The two older results obtained by the third method are worthy of no further mention. Baubigny's work upon the ignition of zincic sulphate is very interesting, but probably incomplete. It will be remembered that the value for copper obtained by the same method was too low, † owing, probably, to the occlusion of sulphuric acid by the cupric sulphate. It is not impossible that a similar error may have crept in here, for the conditions were similar; but it is probable that it is here counterbalanced by the retention of sulphur trioxide by the zincic oxide. In a series of experiments made in this laboratory pure zincic oxide obtained from the carbonate (see p. 163), was ignited to constant weight in an oxidizing atmosphere at a temperature above the fusing point of gold; ‡ it was then dissolved in dilute sulphuric acid which left no residue upon evaporation, and very gradually brought again to the same high temperature. In no case were we able to expel all of the sulphuric acid which we had added. Three experiments are appended:—

* Lord Rayleigh and others.

† Richards, These Proceedings, XXVI. 275.

‡ Four grams of pure gold melted in fifteen minutes from the time of turning on the air blast in the furnace.

Weight of Zincic Oxide before.	Weight of Zincic Oxide after.	Gain.
Grams.	Grams.	Grams.
1.03009	1.03032	0.00023
0.80243	0.80265	0.00022
1.03447	1.03473	0.00026
Average for 1 gram ZnO		0.00025

Gladstone and Hibbert deposited silver in one cell by means of a voltaic current, while zinc was being dissolved from an amalgamated plate in another. Although the experiments are interesting, it would appear from the results of Vanni * and others that the possibility of side reactions makes the strict applications of Faraday's law for the determination of atomic weights of rather doubtful efficacy. One would expect the method adopted to give a result larger than the true one.

Marignac's work upon the chloride of zinc and the double chloride of zinc and potassium is even less satisfactory than his investigations of other chlorine compounds; it merits no further notice.

It is evident from these statements that the three least unsatisfactory determinations are all vitiated to a greater or less extent by constant errors; the work of Morse and Burton by one which tends to lower the result; the work of Gladstone and Hibbert by one which may tend to raise the result; and the work of Baubigny by two which tend to counteract one another. One would expect the atomic weight of zinc to prove in the end equal to about 65.4.

It seemed very desirable to obtain a series of determinations which should be wholly different from any of these; and for this reason zincic bromide was chosen as the starting point of the present research. Additional advantages presented by the use of this substance are the fact of its ready and accurate analysis, and the fact that a determination of the ratio $2 \text{ Ag} : \text{ZnBr}_2$ would bring the element into a series of elements which have been determined by Stas and others with great precision in this way.

* Berichte d. d. Ch. G., XXIV., Ref. 882.

BALANCES AND WEIGHTS.

The preliminary determinations were made upon a long-armed Becker balance with the help of very carefully standardized platinized brass weights. The final determinations were made upon the admirable Troemer balance procured for the research upon copper, and subsequently used for those upon barium and strontium. The weights used in these final determinations were the same as those used in the researches just cited ; they were compared with one another at the beginning and at the close of the research, with satisfactory results. All weighings were made by substitution, the tare weights being vessels as nearly as possible similar to those being weighed ; and all were reduced to the vacuum standard by the usual formula.

THE SPECIFIC GRAVITY OF ZINCIC BROMIDE.

In the course of recent investigations upon the atomic weights so many of the usually accepted specific gravities of hygroscopic substances have been found to be seriously in error, that it seemed advisable to redetermine the constant which influences the reduction to vacuum of the present results.

Pure zincic bromide was dried for a long time at a temperature of 200° , and then fused and heated for a short time at 300° . The pycnometer in which this drying was effected was then stoppered and cooled in a desiccator. Carefully dried toluol having a specific gravity of 0.8646 at 20° , when referred to water at 4° , was used as the liquid to be displaced. Toluol is convenient for the purpose, because so few inorganic substances are soluble in it, and because its volatility is not so great as to cause serious loss during the weighing, but is great enough to allow of the rapid drying of the exterior of the apparatus. The first sample of zincic bromide was made from very pure hydrobromic acid and ordinary pure zinc, and was distilled in an atmosphere of carbon dioxide ; the second was made from the purest electrolytic zinc and the purest bromine. Both samples gave a perfectly clear dilute solution in water after the expulsion of the toluol on the steam bath after the experiment. The decanted toluol left upon evaporation on the steam bath only a trace of residue, which was insoluble in water. Water decanted from this residue gave no trace of precipitation with argentic nitrate ; hence it is evident that zincic bromide is insoluble in toluol. The liquid contained in glass

increases about 0.001 of its apparent volume for each degree of temperature; and the small appropriate correction is applied below.

SPECIFIC GRAVITY OF ZINCIC BROMIDE.

No. of Experiment.	Weight of $ZnBr_2$.	Tempera-ture.	Weight of Toluol displaced.	Water at 40° corre-sponding to Toluol.	Specific Gravity of $ZnBr_2$ at 20° .
	Grams.	Degrees.	Grams.	Grams.	
(1)	3.8856	19.8	0.7960	0.9206	4.220
(2)	11.2394	20.3	2.303	2.664	4.218
Average					4.219

The value 4.22 is used in the work which follows. In this connection it may be of interest to compare the specific gravities of the substances recently determined here.

SPECIFIC GRAVITIES COMPARED WITH WATER AT 4° .

Substance.	Old Values.	Former Experiments.	New Values.	Temperature.
Anhydrous $BaCl_2$	3.85	{ Quincke Favre and Volson Schroeder }	3.86	24°
$BaBr_2$	4.23	Schiff	4.79	24°
$SrBr_2$	3.96	Bödeker	4.22	24°
$ZnBr_2$	3.64	Bödeker	4.22	20°
Crystallized $Ba - Cl_2 \cdot 2H_2O$	3.05±	{ Joule and Playfair Schiff Schroeder }	3.10	24°

PRELIMINARY ANALYSES OF ZINCIC BROMIDE.

Preparation of Zincic Oxide. The zincic bromide used for the first series of experiments was made by the action of pure hydrobromic acid upon pure zincic oxide. For the preparation of the oxide "pure" zinc of commerce was dissolved in pure dilute sulphuric acid, and the solution was allowed to remain over an excess of the metal for several weeks. The filtered solution was acidified with sulphuric acid, warmed, and treated with well washed hydric sulphide, until a considerable mass of pure white precipitate had formed.

The strongly smelling filtrate from this zincic sulphide, now freed from all traces of the most usual metallic impurities, was treated with chlorine water to oxidize any iron or manganese which might be present, and precipitated fractionally with pure sodic carbonate. The first fraction of the precipitate containing traces of iron and manganese was thrown away.

After a thorough washing the second fraction, containing most of the zinc, was dissolved in pure nitric acid, keeping the carbonate in excess. After filtration, the addition of a little ammonic carbonate, and another filtration, the greater part of the zinc present was precipitated by means of ammonic carbonate. When it had been subjected to a thorough washing the basic zincic carbonate was ignited in a double platinum crucible over an alcohol lamp. The oxide thus obtained was washed repeatedly with water, for often an impurity which is held by a wet precipitate may be washed out when the precipitate has been partially decomposed or disintegrated by heat. Artus* has observed that the sodic carbonate occluded in the quantitative precipitation of zinc may be easily removed in this way, and the present experience showed that occluded zinc chloride could be washed away with equal ease. The zinc oxide thus obtained was almost white, with a very faint tinge of yellow; upon solution in nitric acid it gave absolutely no opalescence with argentic nitrate. Its method of preparation made the presence of non-volatile impurities almost impossible, for it was precipitated from a solution containing nothing but zinc, nitric acid, and ammonia.

Preparation of Hydrobromic Acid. This substance was made by the action of bromine on water in the presence of phosphorus. The bromine was purified by the well known method of Stas,† having been dissolved in a saturated solution of potassic bromide holding zinc oxide in suspension, and distilled from this solution after long standing. The bromine, thus freed from chlorine and iodine, was collected under water and redistilled. Red phosphorus was now purified by very fine pulverization under water and by repeated washing of the powder with pure water. According to Stas this method removes every trace of chlorine which may be held by the substance. Our own experience has not been uniformly favorable in this respect, but upon this occasion and several others both the qualitative tests for the absence of chlorine and the quantitative analysis of the hydrobromic acid made with the assistance of well washed phosphorus were satisfactory. The bromine

* Berzelius, *Jahresbericht*, XXIII. 132.

† *Mém. Acad. Belg.*, XLIII. Pt. II. 90, 38.

was allowed to act upon the phosphorus and water with the usual precautions in an apparatus made wholly of glass. The acid thus formed was distilled in five fractions, of which the first consisted chiefly of water and a trace of bromoform. Only the last fraction of the distillate containing perhaps a third of the bromine taken, was used in the work; and this was redistilled with the further rejection of the first and last portions. The remainder was analyzed quantitatively with pure silver in order to test its freedom from chlorine, with very satisfactory results. The silver was prepared, weighed, and dissolved with great care, the precipitate was collected upon a Gooch crucible, and all weighings were reduced to the vacuum standard.

PURITY OF HYDROBROMIC ACID.

No. of Experiment.	Weight of Silver.	Weight of Argentie Bromide.	Per cent of Silver in Argentie Bromide.
(3)	1.86058	3.23884	57.446
(4)	1.72320	2.99983	57.443
Average			57.444
Stas found			57.445

Preparation of Zincic Bromide. For experiments 5 and 6 zincic bromide was made by simply dissolving in a platinum dish the pure oxide in the pure acid described above. For experiment 7 similar zincic bromide was sublimed in a wide glass tube in a current of pure dry carbon dioxide. The next experiment, No. 9, was made with similar zincic bromide prepared wholly in glass and not sublimed. A large portion of the substance was then prepared by exact neutralization and evaporation in a platinum dish, a strip of pure zinc was added to precipitate a trace of platinum,—which had been dissolved because of the presence of traces of oxidized nitrogen in the oxide,—and the whole was subjected to crystallization. The mother liquor served for analysis 8, and the pure white crystals for the third series of preliminary determinations (Experiments 10, 11, 12, and 13).

Preparation of Silver.—This substance was prepared by the method described in a recent paper upon the atomic weight of barium.*

Pure argentie chloride was reduced by means of pure sodic hydrate and invert sugar, and the metal was washed and fused in a gas flame

* These Proceedings, XXVIII. 22; XXIX. 64.

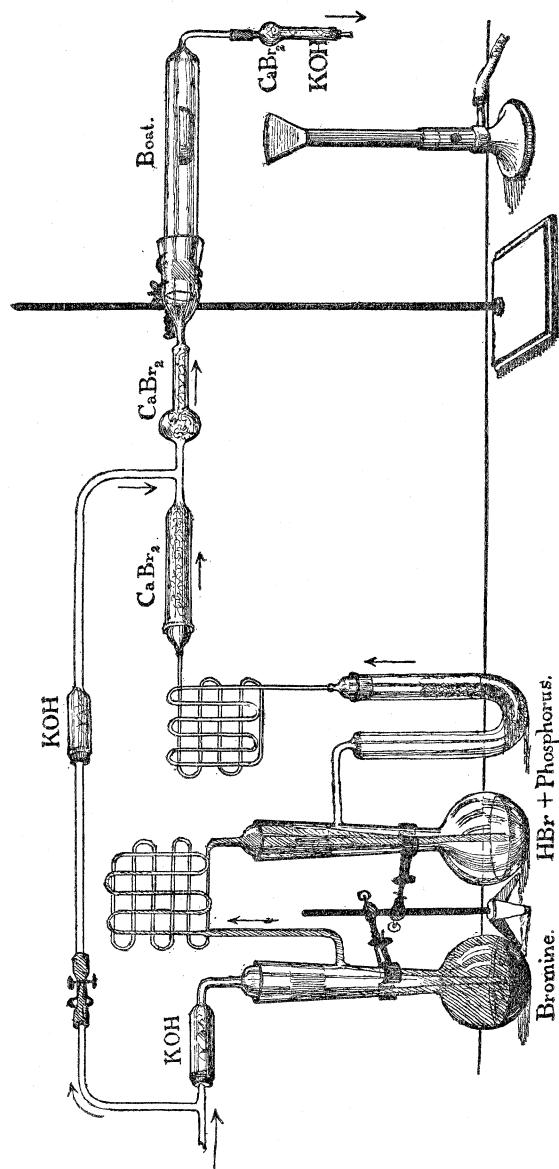
upon charcoal. The lumps thus obtained were dissolved in pure nitric acid and precipitated by electrolysis. The beautiful crystals of electrolytic silver were rapidly fused upon cupels of sugar charcoal * in the flame of illuminating gas, and cooled in a reducing atmosphere. Such silver is essentially identical with the much more carefully prepared metal used in the final experiments, and gives every evidence of being pure within two or three parts in a hundred thousand.† A solution of argentic nitrate through which over fifty grams of such silver had passed by electrolysis, was found upon suitable treatment to yield only half a milligram of baric sulphate; hence the silver could not have contained more than two parts of sulphur in a million.

Preparation of other Materials. — Nitric acid was repeatedly distilled, the last portion of the distillates being used. It is needless to say that it was wholly free from halogens. The sulphuric acid used for analytical purposes was distilled with great care; that used for desiccators was boiled with a little ammonic sulphate. The water used in the preliminary determinations was twice distilled in a tin condenser. In order to avoid the introduction of chlorine, carbon dioxide was prepared at first from acid sodic carbonate and sulphuric acid, later from dilute nitric acid and marble. Nitrogen mixed with argon was prepared by passing a mixture of air and ammonia over red-hot copper. Both gases were very thoroughly washed.

Method of Analysis. — The necessity of driving out every trace of water from the substance to be analyzed was the precaution upon which most labor was expended. The low boiling points of zincic bromide makes it possible to distil the substance easily in a hard glass tube. Accordingly, for the first series of very crude experiments pure zincic bromide was distilled in a tube provided with bulbs, which were sealed off when filled. In order to obviate the introduction of an error from the additional weight of the atmosphere of carbon dioxide in which the distillation took place, the bulbs were heated to about 120° at the moment of sealing. The bulbs were weighed after scratching them upon each end with a file; and after the zinc bromide had been dissolved out the glass was weighed alone. The bromine present was weighed as argentic bromide, and the atomic weight of zincic was calculated from the ratio of argentic and zincic bromides. The more trustworthy results ranged from 65.40 to 65.54, with an average of 65.47; but it was clear that the method admitted of too many possibilities of error to yield satisfactory results.

* These Proceedings, XXIX. 65.

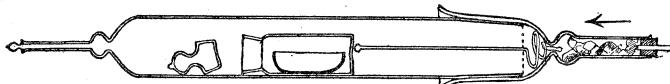
† Ibid.



APPARATUS FOR FUSING ZINCIC BROMIDE.

Pure dry nitrogen and argon enter the apparatus through the tube at the left. The arrangement for preparing this mixture is not shown. Upon closing the pinchcock in the upper left hand corner the gases are driven through the flasks and charged with dry hydrobromic acid; upon opening the pinchcock the hydrostatic pressure causes the gases to flow through the upper short cut tube and effectually to sweep out the acid from the fusion tube. This latter tube, containing the boat in which the zincic bromide is fused, is at the right of the figure.

Hence the method which answered well in the recent analysis of strontic bromide* was adopted here. The pure recrystallized or sublimed zincic bromide was placed in a platinum boat and kept for some time in an atmosphere of pure dry nitrogen charged with pure hydrobromic acid. It was found that in this way all the water could be expelled from the salt without the introduction of a trace of oxybromide; indeed, zincic bromide which by rapid heating in the air had been partly decomposed could be speedily brought back to its normal condition by fusion in the atmosphere of dry dilute hydric bromide. The presence of the insoluble oxybromide is easily detected by dissolving the bromide in large amounts of water; in every case the bromide used in the analyses below gave an absolutely clear solution. Baric and strontic bromides ignited in the same way give solutions which are absolutely neutral to methyl orange and phenol phthalein; hence it is most likely than the zincic bromide, which does not admit of similar alkalimetric testing, is also quite normal. For the details the paper upon strontium must be consulted, but a sketch of the apparatus will probably suffice. (See preceding page.) In the present case hydrogen could not be added to the nitrogen for fear of reducing some of the zincic bromide; but no trouble was experienced from corrosion of the boat. When the substance had been kept for some time in a state of tranquil fusion, and had just solidified, the boat was quickly slid into a weighing tube which was in its turn placed in the automatic desiccator tube shown below. After the tube and boat



had been heated to about 200° for some time in a current of pure dry air, the desiccator tube was raised to a vertical position, the stopper being thus allowed to fall into place.

After weighing, the pure zinc bromide was dissolved in water and precipitated by means of a slight excess of very carefully weighed pure silver in very dilute solution. The argentic bromide was collected upon a Gooch crucible, the shreds of asbestos carried through (0.05 to 0.20 milligram) were collected upon a very small fine filter, and the total weight of the argentic bromide thus obtained gave one ratio upon which to base the atomic weight of zinc. In the third series the filtrate

* These Proceedings, XXX. 369.

was all evaporated to very small bulk, and the excess of silver precipitated by hydrobromic acid and weighed upon a Gooch crucible in the same way as the other portion of argentic bromide. By subtracting this excess from the total silver originally weighed out, the weight of silver equivalent to the zincic bromide could be easily found. Great care was taken to exclude daylight, and to carry out all the precautions necessary in accurate work. The data are given below.

SECOND SERIES.

THE RATIO OF ZINCIC BROMIDE TO ARGENTIC BROMIDE.

No. of Analysis.	Weight of Zincic Bromide.	Weight of Argentic Bromide.	Atomic Weight of Zinc.
	Grams.	Grams.	
(5)	1.69616	2.82805	65.469
(6)	1.98198	3.30450	65.470
(7)	1.70920	2.84949	65.487
(8)	2.35079	3.91941	65.470
(9)	2.66078	4.43751	65.400
Average			65.459

THIRD SERIES.

THE RATIO OF ZINCIC BROMIDE TO SILVER AND ARGENTIC BROMIDE.

No. of Analysis.	Weight of Zincic Bromide.	Weight of Silver.	Weight of Argentic Bromide.	Atomic Weight of Zinc from $\text{Ag}_2 : \text{ZnBr}_2$.	Atomic Weight of Zinc from $2\text{AgBr} : \text{Zn Br}_2$.
	Grams.	Grams.	Grams.		
(10)	2.33882	2.24063	3.90067	65.409	65.400
(11)	1.97142	1.88837	3.28742	65.444	65.434
(12)	2.14985	2.05971	3.58539	65.396	65.402
(13)	2.00966	1.92476	3.35074	65.472	65.463
Average			65.430	65.425	

The second series of results, excepting the last determination, is undoubtedly affected by the presence of water in the zincic bromide; for the methods of drying and transference had not been perfected. The third series was much more carefully made, but even here there was a possibility of the retention of a small amount of water in some of the analyses, hence this result also is probably somewhat too high.

The results of the four analyses of the third series give the following figures for the per cent of silver in the bromide: 57.443, 57.443, 57.447, and 57.443. The mean of these results is 57.444; Stas having found 57.445. It will be remembered that the hydrobromic acid from which the zincic bromide was made gave precisely similar results. This identity proves that the analytical work was without fault, and that argentic bromide does not possess the slightest tendency to occlude zincic bromide when precipitated from dilute solutions. The analysis of the hydrobromic acid proved that the material was free from chlorine and iodine.

Accordingly the rather large variations in the results must be due wholly to the original condition of the samples of zincic bromide. It remained therefore, to make a final series of determinations upon zincic bromide from which water should have been absolutely excluded; and since one of us was unfortunately called away, this series was made by the other alone.

FINAL SERIES OF DETERMINATIONS.

BY THEODORE WILLIAM RICHARDS.

One determination of the final series, No. 17, was made with the old zincic bromide in the new apparatus. The others were all made from new material prepared from electrolytic zinc and pure bromine, instead of from zincic oxide and hydrobromic acid. The electrolytic zinc was prepared with great care in the following manner: An excess of "pure" zinc was treated with somewhat dilute pure sulphuric acid at 80° until upon dilution a marked amount of basic salt was formed. About three hundred grams of zinc had been dissolved; and this diluted solution was allowed to stand for many hours in contact with the zinc and the basic salt. After filtering, clean pieces of zinc were added to the solution; and no further metallic precipitate formed upon the zinc. The solution was then decanted and treated with a small amount of sulphuric acid and much hydric sulphide. After some time the pure white precipitate was separated by decantation and filtration, and the solution was oxidized by an excess of pure chlorine. To this solution was then added enough very pure sodic carbonate to form a slight precipitate, and the mixture was allowed to stand several days with occasional stirring. The pure white precipitate, which must have contained any trace of iron remaining, was filtered off, and the sulphate of zinc was crystallized three times successively from hot water.

The solution of the last crystals was allowed to stand for two days over several grams of the purest crystalline electrolytic zinc in a large platinum dish. At the end of that time the solution contained some basic salt, but the dish showed no sign of a metallic coating. The solution was filtered, treated with an excess of freshly distilled ammonia, and electrolyzed. A thin rod of very pure zinc served as the negative pole, and a platinum wire as the positive. Six decomposing cells were run simultaneously on a shunt from a fifty-volt dynamo which was being used for charging a storage battery. The current in each decomposing cell varied from one to one and a half amperes,— if a much stronger current was used the cells became too warm. As Ramsay and Reynolds * have suggested, it is advisable to remove the remarkably beautiful crystals from time to time as they grow; for this purpose a bent five-pronged glass fork made from a heavy rod was found very useful. The crystals were washed with ammonia until the washings were absolutely free from sulphuric acid, then with pure very dilute hydrobromic acid, and finally with much pure water. About forty grams of pure zinc thus formed were treated with an excess of pure bromine, which had been shaken with an alkaline bromide in aqueous solution, dissolved in concentrated calcic bromide, precipitated by water, and distilled under dilute pure hydrobromic acid. The Jena glass flask in which the combination took place was cooled during the reaction. The red solution was filtered in a glass funnel through asbestos, and the excess of bromine, together with any trace of iodine which may have been present, was driven off by leaving the Jena flask upon the steam bath for some time in a very much inclined position. The diluted colorless solution was evaporated to small bulk, and the greater part of it was subjected to fractional crystallization by cooling to zero. A portion which had crystallized twice successively, from water was labelled (A), and another portion, the extreme mother liquor remaining from two crystallizations was labelled (C). Sample (B), the intermediate fraction, was not used in these experiments, as (A) and (C) were proved to be identical.

Before analysis both (A) and (C) were subjected either to distillation or to sublimation. The sublimation was carried on in the lower part of a platinum retort, to which had been fitted closely a glass adapter for conducting the current of pure dry carbon dioxide. The substance to be sublimed was contained in a small platinum crucible fitted with a wire handle, by which it could easily be raised, lowered, or removed.

* *Loc. cit.*

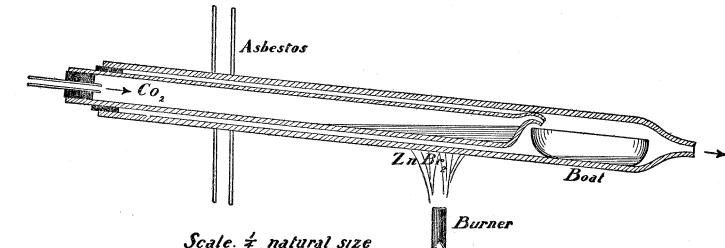
The adapter was so arranged that the current of gas came as closely as possible in contact with the crucible, and so that any zinc bromide which might condense in a liquid form upon the glass, and thus run the risk of taking alkali from it, must return to the crucible and be redistilled. The sectional drawing will give a clearer idea of the arrangement.

Two powerful Bunsen burners supplied heat from below, impinging upon a porcelain dish which fitted closely to the bottom of the retort

and protected the platinum. The gases from the flame were diverted by a large diaphragm of asbestos board. By means of this arrangement it is possible to sublime about half a gram of zincic bromide an hour; the crystals are exceedingly beautiful, and give every evidence of great purity.

Instead of being sublimed, some of the pure salt was distilled in a current of carbon dioxide. For this purpose a medium sized tube of the hardest glass was drawn out so as to serve for a small retort, and this was encased in a larger hard glass tube, from which it was separated

by several pieces of platinum foil. A platinum boat, into which was directed the drawn out and turned over point of the inner tube, served as the receiver. Here again a diagram must assist the explanation.



The zinc bromide thus distilled possessed a peculiarly brilliant white lustre; in no case did the boat lose or gain the twentieth of a milligram in weight during the distillation.

The attempt was made also to distil the bromide in a vacuum, but the reduction of the pressure lowered the boiling point too nearly to the proximity of the melting point for convenient manipulation.

In this connection it may be well to state the atomic weight of zinc obtained from these specimens, in order to show their identity. The details of these figures are given later.

From the substance used in the preliminary determinations (Expt. 17)	65.410
From new substance not crystallized from water but distilled in carbon dioxide (Expt. 14)	65.403
From extreme mother liquors from crystallization (C) sub- limed in carbon dioxide (Expt. 18)	65.404
From purest crystals (A), twice crystallized from water and sublimed (Expt. 15, 19).	65.404
From purest crystals (A) twice crystallized from water and twice distilled in carbon dioxide (Expt. 16)	65.398
Average	Zn = 65.404

Silver.—The silver used in the final determinations was repeatedly purified by the methods already described. Finally the beautiful electrolytic crystals were fused in a small crucible of pure lime in a vacuum. In this way the metal may be obtained in the purest possible state, for if it is distilled according to Stas there is always danger of impurity from the oxygen and illuminating gas or hydrogen used in the oxygen blowpipe.

Other Materials.—The acids were purified in the usual fashion and the greater part of the water used was only distilled twice, rejecting the first portions. For experiment 16, all the water used was distilled three times, once over potassic permanganate. Of course the platinum condenser which has been already described served for all of these distillations.*

Phosphoric pentoxide was sublimed in a stream of pure oxygen. Since the presence of oxides of nitrogen in carbon dioxide might assist the partial decomposition of zincic bromide, nitric acid was rejected as a means of decomposing marble, and very dilute hydrochloric acid was used instead. The gas was purified by passing through a solution of sodic hydric carbonate, long tubes containing argentic nitrate, and much pure water. Since the last tube containing water gave absolutely no test for chlorine after over a hundred litres of the gas

* These Proceedings, XXX, 380.

had passed through it, one may safely assume that the purification was sufficient. The gas was dried by means of sulphuric acid and phosphoric pentoxide.

Method of Analysis. — Perhaps the best method of explaining the method of analysis is to give a detailed description of a single determination; and for this purpose Analyses 15 and 19, in which both silver and argentic bromide were weighed, will best serve.

The very pure sublimed zincic bromide was pressed into a platinum boat; and the boat was placed in a tube of hard glass, which had been ground into another tube designed to contain a weighing bottle. The apparatus consisted essentially of a combination of the two pieces of apparatus shown upon pages 167 and 168; it was devised for a research upon the atomic weight of magnesium now being carried on by Messrs. Richards and Parker, and it will be described in full when that investigation is published. With the help of this apparatus it was possible to heat the zincic bromide to any temperature below its boiling point in an atmosphere of pure dry air, pure dry carbon dioxide, or pure dry carbon dioxide charged with hydrobromic acid; and these gases could be changed at will merely by the opening and closing of stopcocks. When the heating had been continued for the desired length of time, it was possible to push the boat into the weighing bottle and to stopper the weighing bottle very tightly in a perfectly dry atmosphere, without the least chance of the absorption of moisture from the outside air. All the apparatus which could possibly come into contact with bromine or hydrobromic acid was made of glass, with ground glass joints and glass gridirons for convenient refilling.

The zincic bromide was heated very gradually at first in an atmosphere of carbon dioxide which had been dried by passing over sulphuric acid, fused zincic bromide, and phosphorus pentoxide. If heated very gradually in this way, zincic bromide may be almost wholly dehydrated without loss of bromine; but a basic bromide is certain to form if the heating is rapid. When all of the apparent water had been expelled from the substance and its containing tube, dry hydric bromide was added to the carbonic dioxide, and the temperature was gradually raised to the fusing point of zincic bromide. The bromide was kept at a temperature just above its melting point for about an hour; during this time perhaps a tenth of the substance sublimed in the exit end of the "combustion" tube, — rendering the drying tube — which had been ground on to protect the exit — unnecessary. It was assumed that at the end of an hour the fused zincic bromide must be as free from water and from basic salt as it was

possible to obtain it; accordingly, the temperature was allowed to fall to about 200° , and the current of dry hydrobromic acid was stopped. Soon air—dried by means of sulphuric acid, fused potash, and phosphorus pentoxide—was substituted for the carbon dioxide, the temperature being allowed to fall to about 150° to avoid any possible decomposition of the zincic bromide; and this current of air was continued for several hours until long after every trace of hydrobromic and carbonic acid had been swept away. In order to “make assurance doubly sure” the whole length of the tube, weighing-bottle and all, was heated to 100° or more several times, in order to prevent any possible occlusion of acid. When all was in readiness, the warm boat was pushed by means of a long glass rod into the weighing bottle, and the bottle was stoppered with the help of the same rod. The apparatus was then pulled to pieces, the closed bottle was transferred at once to a tight desiccator, and after a suitable rest of several hours, it was weighed with all possible care. The various weighings are tabulated below.*

	Common Weights Right-hand pan,	Tare: Standard Weights, Left-hand Pan by Substitution.	Standard Weights corrected.
	Grams.	Grams.	Grams.
Weight of boat beforehand	7.7693	7.76937	7.76932
Weight of boat + bottle	19.9757	0.00872	0.00372
The same + ZnBr_2 after seven } hours' cooling	25.2889	5.26754	5.26747
After two hours more	25.2889	5.26754	5.26747
After two hours' standing in } balance	5.26757	5.26750
Weight of boat after experiment	7.7693	7.76938	7.76938
Boat + bottle afterward	19.9757	0.00875	0.00375
Gain of boat	0.00001
Gain of boat + bottle	0.00003
Average tare of boat + bottle } + ZnBr_2	5.26748
Average tare of boat + bottle	0.00373
Weight of ZnBr_2 in air	5.26375
Correction to vacuum 20° and } 762 mm.00074
Weight of ZnBr_2 in vacuum	5.26449

Before having been treated with water, the bottle and boat were allowed to stand for twenty hours in somewhat moist air. During

* For detailed method see These Proceedings, XXVIII. 5.

that time they gained only two tenths of a milligram, showing that the diffusion of moisture through the stopper was very slow. In order to prove the efficiency of the drying and fusing apparatus, the bottle with its contents were returned to it, and the stopper was removed by means of a wire while a current of dry air was allowed to pass through the whole apparatus. This current was continued for half an hour, the boat and bottle being warmed to about 120° . After suitable cooling the substance was found to have lost one tenth of a milligram, being one tenth heavier than it was in the first place. These weights were not included above in order to avoid complications; they do not belong necessarily to the analysis, but merely serve to show that the apparatus was wholly sufficient for its purpose.

The boat and its contents were conveyed with great care to a large Bohemian beaker, and the weighing bottle was rinsed out many times with the purest water. When the zincic bromide had wholly dissolved, the perfectly clear solution was transferred through a large funnel to the glass stoppered Erlenmeyer flask intended to serve for the precipitation. The boat was easily washed by allowing it to rest in the funnel, and of course beaker and all were rinsed with the most scrupulous care. The total volume of the thus diluted zincic bromide amounted to about two hundred and fifty cubic centimeters.

The silver to be used for the precipitation weighed 5.04328 grams in the air, or 5.04313 grams in vacuum. It was dissolved in ten cubic centimeters of nitric acid diluted with water in a large flask provided with a bulb tube, and the absolutely clear solution was freed from lower oxides of nitrogen by standing upon the steam bath. The contents of the bulbs, usually containing only a few hundredths of a milligram of silver, were washed back into the flask, and the whole was diluted to about half a litre.

The addition of the argentic nitrate to the zincic bromide took place in the dark-room,* and great pains were taken to prevent exposure of the materials to anything but non-actinic light from this time until the final weighing of the argentic bromide. Of course every trace of silver was washed into the flask containing the zincic bromide. After the whole had been very thoroughly shaken and allowed to stand for several days, 0.21 cubic centimeter of hydrobromic acid (one cubic centimeter was equivalent to a milligram of silver) failed to produce an evident precipitate, even when the solution was lighted by a brilliant condensed beam of yellow light. On the other hand, 0.60 cubic

* See previous papers upon barium and strontium.

centimeter of an equivalent solution of silver produced an evident cloudiness. 0.40 cubic centimeter more also produced a cloud. Still 0.20 cubic centimeter gave a very faint indication of opalescence, after a long time, and finally 0.21 gave no trace. On titrating back with hydrobromic acid, it was necessary to add 1.21 cubic centimeters more before the point was reached where an extra 0.20 produced no precipitate. The total amount of silver solution added was then 1.41 cubic centimeters, or 0.21 to precipitate the first amount of hydrobromic acid added, 0.21 to show that all the bromine was precipitated, and 0.99 to correspond to the true amount of silver to be added in order to attain the end point; while the total amount of hydrobromic acid added to reach the end point in the other direction was 1.42 cubic centimeters, an amount which must be subtracted from the amount of silver added. Hence, since the true amount of silver corresponding to the zincic bromide is the mean between the amounts found by titrating in opposite directions,* we obtain it as follows:—

AMOUNT OF SILVER REQUIRED.

	Grams in Vacuum.
Titrating with argentic nitrate .	$5.04313 + 0.00099 = 5.04412$
Titrating with hydrobromic acid	$5.04313 + 0.00141 - 0.00142 = 5.04132$
Average: silver required	5.04362

Since it is hardly probable that the end point may be obtained by this method more nearly than the tenth of a milligram, the last figure is omitted below.

If, as is probable, the action of silver and hydrobromic acid in preventing the solution of silver bromide resembles the action of silver and hydrochloric in precipitating solutions of silver chloride (Stas), the difference between the end points (1.00 milligram of silver) corresponds to six times the amount of argentic bromide dissolved. That is, this amount must be about $\frac{1}{6}^{74}$ or 0.29 milligram in 0.85 liter of a solution containing two or three cubic centimeters of nitric acid and about five grams of zincic nitrate.

In order to precipitate all the bromine, four milligrams more of argentic nitrate were added to the solution and the whole was very

* These Proceedings, XXVIII. 24, XXIX. 74, XXX. 384.

vigorously shaken. After a day or two the mixture was filtered through a weighed Gooch crucible and the precipitate was shaken and allowed to stand with many successive portions of water containing five milligrams of argentic nitrate to the litre. It was finally transferred quantitatively to the crucible, washed with pure water to remove the traces of argentic nitrate and dried at 160° in a porcelain drying oven in a stream of air purified by passing over sulphuric acid and potash. The two litres of filtrate were allowed to stand until the shreds of asbestos had settled; and these were collected upon three thicknesses of the best filter paper, ignited and weighed. The main body of the precipitate was transferred to a porcelain crucible, weighed, fused in a porcelain oven, and weighed again. Below are the data.

	Common Weights.	Standard Weights by Substitution.	Standard Weights corrected.
	Grams.	Grams.	Grams.
Gooch crucible alone	18.4812	0.22840	0.22840
Gooch crucible + AgBr	27.2633	9.01052	9.01050
Argentic bromide in air	· · · · ·	· · · · ·	8.78210
Correction to vacuum	· · · · ·	· · · · ·	0.00039
Chief mass of argentic bromide in vacuum	· · · · ·	· · · · ·	8.78249
Porcelain crucible + AgBr	25.6757	8.37781	
The same after fusion	25.6755	8.37760	
Loss on fusion	· · · · ·	0.00021	0.00021
Crucible + ash + asbestos	15.2857	0.05284	
Crucible	15.2853	0.05226	
Ash + asbestos	· · · · ·	0.00058	
Ash of three filters	· · · · ·	0.00012	
Asbestos	· · · · ·	0.00046	0.00046
Total weight of AgBr	· · · · ·	· · · · ·	8.78274
Subtract amount corresponding to 1.42 + 0.20 = 1.62 c.c. HBr solution . . }	· · · · ·	· · · · ·	0.00282
Argentic bromide corresponding to zincic bromide	· · · · ·	· · · · ·	8.77992

Thus 5.26449 grams of zincic bromide correspond to 5.0436 grams of silver and 8.77992 grams of argentic bromide. If bromine and silver are taken as 79.955 and 107.93 as usual, the atomic weights of zinc computed from these ratios are identical, — 65.404. Since this is the case, of course the per cent of silver found in argentic bromide $\frac{5.0436}{8.77992} \times 100$ is identical with that obtained by Stas, or 57.445.

In no one of the other determinations were both silver and argentic bromide determined, hence the others were simpler in execution, although essentially the same in principle. The end point in analysis 17 was probably not determined more nearly than two tenths of a milligram, while that in analysis 19 was determined by the nephelometer * much more accurately even than in the detailed determination. Indeed this value was so accurate that the hundredths of a milligram may have some significance, although the weights taken were so large. The data of all these final determinations are given below.

FINAL DETERMINATIONS.

THE RATIO OF ZINCIC BROMIDE TO SILVER.

Number of Analysis.	Weight of Zincic Bromide.	Weight of Silver.	Ratio. $\frac{\text{ZnBr}_2}{2\text{Ag}}$	Atomic Weight of Zinc.
(14)	Grams. 6.23833	Grams. 5.9766	104.379	65.403
(15)	5.26449	5.0436	104.380	65.404
(16)	9.36283	8.9702	104.377	65.398
Average			104.379	65.402

THE RATIO OF ZINCIC BROMIDE TO ARGENTIC BROMIDE.

Number of Analysis.	Weight of Zincic Bromide.	Weight of Argentic Bromide.	Ratio. $\frac{\text{ZnBr}_2}{2\text{AgBr}}$	Atomic Weight of Zinc.
(17)	Grams. 2.65847	Grams. 4.43358	0.599622	65.410
(18)	2.30989	3.85149	0.599606	65.404
(19)	5.26449	8.77992	0.599606	65.404
Average			0.599611	65.406

From the first ratio, if $0 = 16$

$$\text{Zn} = \underline{\underline{65.402}}$$

From the second ratio, if $0 = 16$

$$\text{Zn} = \underline{\underline{65.406}}$$

Average, if $0 = 16$

$$\text{Zn} = \underline{\underline{65.404}}$$

If $0 = 15.96$

$$\text{Zn} = \underline{65.240}$$

If $0 = 15.88$

$$\text{Zn} = \underline{64.912}$$

* These Proceedings, XXX. 385.

In this determination the only serious possibility of error is that the zincic bromide may have contained a lingering trace of water in spite of the elaborate precautions adopted to secure its absence. It is hoped that before long a determination of the zinc as well as of the bromine in zincic bromide may be made in this laboratory, furnishing evidence upon this point. However, since the figure given above agrees closely with the probable corrected result of Morse and Burton's investigation, as well as with the somewhat incomplete determinations of Baubigny and Gladstone and Hibbert, the value 65.40 may be safely adopted for the present as the most probable value of the atomic weight of zinc.